

Universal Dielectric Enhancement from Externally Induced Double Layer Without ζ -potential

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arXiv:1510.06724v3 [physics.class-ph] 11 Apr 2016

Abstract

Abstract: Motivated by recent experiments showing over 10^4 -fold increase in induced polarization from electrochemically inert, conducting materials in dilute saline solutions, we theoretically demonstrate a new mechanism for dielectric enhancement, in the absence of ζ -potentials at interfaces between non-insulating particles and an electrolyte solution. We further show that the magnitude of such enhancement obeys universal scaling laws, independent of the particle's electrical properties and valid across particle shapes: for a dilute suspension of identical, but arbitrarily shaped particles of a linear dimension a and volume fraction f , as $\omega \rightarrow 0$ the effective real dielectric constant of the mixture is enhanced from that of water by a factor $1 + f (P_r + (a/\lambda)P_i)$, and the frequency-dependent phase shift of its impedance has a scale-invariant maximum $f \Theta$ if particles are much more conductive than the solution. Here λ is the solution's Debye length and P_r, P_i, Θ are dimensionless numbers determined solely by the particles' shape. Even for a very dilute electrolyte solution (e.g. 10^{-3} molar), sub-mm sized particles, at volume fraction $f = 0.1$, can give a 10^4 -fold dielectric enhancement, producing an easily observable phase shift maximum in a simple impedance measurement. We also derive frequency cutoffs as conditions for observing these enhancements, showing that insulating particles produce no enhancement without ζ -potential. To prove these results for particles of arbitrary shapes, we develop a physical picture where an externally induced double layer (EIDL), in contrast to the Guoy-Chapman double layer on interfaces with significant ζ -potentials, dominates the low-frequency dynamics and produces dielectric enhancement.

Significance Statement: Dielectric enhancement is a striking and technologically important phenomenon in complex fluids: the introduction of a small amount of suspended particles can boost the low-frequency dielectric constant of an electrolyte solution by many orders of magnitudes. It is crucial for understanding dielectric responses in systems as disparate as gold particles in cytosol and mineral deposits in geological exploration. Dielectric enhancement is traditionally thought to be caused by large surface potentials on solid-fluid interfaces. Our theory suggests that this phenomenon is more widespread and fundamental in nature. We show that even without electrochemically active surfaces, a dilute suspension of non-insulating, arbitrarily shaped particles in an electrolyte solution can produce a huge low-frequency dielectric enhancement that obeys universal scaling laws.

In recent experiments aiming at designing contrast agents, intriguing preliminary data suggest that a dilute (volume fraction $f \leq 0.1$) suspension of sub mm-sized particles in a dilute electrolyte solution can produce real dielectric constant over 10^4 times that of the water. These non-metallic conductive particles are not known to attract large surface charges and are chemically inert in the solution. These data are unexpected in the current theoretical framework for dielectric enhancement, underlying significant gaps in our understanding of this important phenomenon in a seemingly simple physical system.

At low-frequency (ω) where the depth of penetration is large, the conductivity and dielectric measurements have great potential as diagnostic probes into complex and hard to reach geometries like human bodies or porous media. For example, both noble metal particles [1] and semiconductor quantum dots [2], functionalized with antibodies and selectively enriched in particular types of cells or organelles, have been used as contrast agents and biosensors [3–5]. Beyond traditional optical probes, they may hold promise for noninvasive imaging applications like electrical impedance tomography [6]. As another example, in geological exploration, shale oil and gas deposits have semiconducting pyrites inclusions and the latter can be detected by geophysical exploration techniques [7]. Artificially introduced contrast agents, mixed with saline fluids injected to wells, are being actively explored for uses in conductivity measurements.

Most theoretical explanations for dielectric enhancement to date rely on the Gouy-Chapman double layer created by a large ζ -potential and surface charges on the solid-solution interface [8–13]. This is natural because they largely focus on experiments with *insulating* particles [14–16], which we show below to be incapable of producing enhancement without ζ -potentials. But many contrast agents in medicine and engineering, not to mention natural mineral deposits, are semiconducting or conducting. To our knowledge, only Wong [17] explicitly considered dielectric enhancement in the absence of ζ -potential in the special case of fully conducting, ideally *non*-polarizable metallic spheres. However, he included an amalgam of ion species both with and without Faradaic currents from redox reaction [18, 19], making his model needlessly complex and his results difficult to interpret. Thus the simplest but crucial zeroth order “model organism” of electrolyte solution-based complex fluid, where *ideally polarizable* solid-fluid interfaces have *no* ζ -potential and *no* redox reaction, has been curiously under-investigated in the literature.

Here we study such a model that strips the physics of dielectric enhancement to its

bare essentials, with neither ζ -potential nor Faradaic current. We show that a dilute suspension such particles, made from a non-insulating material, suffices to produce dielectric enhancement, the magnitude of which follows a universal scaling law whose parameters are determined solely by the *shape* of the particles. Due to the simplicity of our model, we are able to demonstrate this enhancement for particles of *any* shapes. We further derive conditions for observing enhancement and show that, for particles much more conductive than the solution, there is a significant, *scale-invariant* maximum in the frequency-dependent phase shift in impedance measurements.

I. GOVERNING EQUATIONS AND BOUNDARY CONDITIONS

Consider electrically uniform solid bodies or immiscible fluid (henceforth simply referred to as “solid”) submersed in an electrolyte solution as suspended particles or droplets. We assume the solid bodies are smooth and convex, and have aspect ratios not too far from one (*i.e.* they are not needle- or disk-shaped). An external electric field $E_0 \exp(i\omega t)$ in the \hat{z} -axis drives the charge dynamics of the system.

We assume that the ζ -potentials on all interfaces are small. In the online SI, we show that our analysis and results remain valid as long as the ζ -potential $\psi_\zeta \ll k_B T/e$, such that the it does not significantly alter the equilibrium ion densities distributions $N_\pm = N_0 e^{\mp e\psi_\zeta/k_B T} \approx N_0$. This condition can be satisfied by natural materials such as oxidized pyrite [20], as well as by materials whose ζ -potential can be tuned by the pH of the solution [21].

To emphasize physics and simplify notations, we assume the electrolyte solution contains a single species of cations and anions, with charges $\pm e$, and that they share the same diffusion coefficient D . In the online SI, we prove that our results continue to hold for the cases of asymmetric ions, as long as the fluid is charge-neutral when $E_0 = 0$.

The electric potential throughout the system is governed by Poisson’s equation. The solids are uniform, so the potential inside them obeys Laplace’s Equation. In the solution, Poisson’s equation reads

$$\nabla^2 \psi(\vec{r}, t) = -\frac{\rho(\vec{r}, t)}{\epsilon'_w \epsilon_0}; \quad \rho(\vec{r}, t) = e(N_+(\vec{r}, t) - N_-(\vec{r}, t)) \quad (1)$$

Here N_\pm are the number densities of the ions in the solution, ψ is the potential in the fluid and ϵ'_w is the *static* relative permittivity of water.

The motion of ions in the liquid is characterized by three density currents: a diffusive current driven by ion density gradients, a conductive driven by the electric field and a hydrodynamic current from ions being carried by the macroscopic motion of the solution itself.

Without significant ζ -potential and surface charge on solids, the net charge density in the solution is due entirely to the external field. Thus, the electrokinetic flow given by the Helmholtz-Smoluchowski equation [22] is proportional to E_0^2 . In the online SI we show that the ionic current carried by such an electrokinetic flow is much smaller than the conductive current, which is proportional to E_0 , and can be safely ignored in the low-frequency and low field linear limit.

Thus, the ionic currents in the solution consist of diffusive and conductive parts, related by the Einstein relation. The ionic current densities and the corresponding ion number conservation equations are:

$$\vec{j}_{\pm}^N = -D \left(\vec{\nabla} N_{\pm} \pm \frac{eN_{\pm}}{k_B T} \vec{\nabla} \psi \right), \quad \vec{\nabla} \cdot \vec{j}_{\pm}^N(\vec{r}, t) = -\frac{\partial N_{\pm}(\vec{r}, t)}{\partial t} \quad (2)$$

Combining the Poisson Equation Eq. 1 and charge conservation Eq. 2 produces three coupled non-linear partial differential equations for N_{\pm} and ψ_L . At a small enough driving field E_0 we can divide the ion densities into a background charge density $N_{\pm}^0 = N$ for the ions at $E_0 = 0$ and small perturbations due to E_0 : $N_{\pm} = N + n_{\pm}$. Two crucial assumptions, that $n_{\pm} \ll N$ and $\vec{\nabla} N \approx 0$, the latter due to the smallness of the ζ -potential and the insignificance of the double layer when $E_0 = 0$, lead to the linearization and simplification of the Eq. 2:

$$\vec{\nabla} \cdot \vec{j}_{\pm} = i\omega n_{\pm}, \quad \vec{j}_{\pm} = -D \left(\vec{\nabla} n_{\pm} \pm \frac{eN_0}{k_B T} \vec{\nabla} \psi \right), \quad \nabla^2 \psi = -\frac{e(n_+ - n_-)}{\epsilon_0 \epsilon'_w}. \quad (3)$$

We show in the online SI that the condition for linearization is simply $eE_0 a \ll k_B T$, where a is the linear dimension of the solid particles. This condition means, roughly, that the ion densities are not changed greatly from equilibrium values by the driving field, similar in spirits to the condition listed above for ignoring the ζ -potential. Even for mm-sized particles, this condition is easily satisfiable.

For the boundary conditions on a solid-solution boundary Σ , either the ideally polarized or the non-polarizable Butler-Volmer [18]/ Chang-Jaffe [23] boundary conditions (BCs) can be adopted. In this paper we study the former, and in another work we show that results

here can be generalized to the latter. We thus assume ions neither penetrate nor undergo redox reactions on the interface (ideally polarizable), and thus the normal ionic current vanishes on Σ :

$$\hat{u} \cdot j_{\pm}|_{\Sigma} = 0 [\mathbf{a}], \psi_S = \psi [\mathbf{b}], \hat{u} \cdot \vec{\nabla} \psi_S = c \hat{u} \cdot \vec{\nabla} \psi [\mathbf{c}], c = \frac{i\omega\epsilon'_w\epsilon_0}{\sigma_s + i\omega\epsilon_0\epsilon'_s} \quad (4)$$

Here we also list the standard BCs matching the potentials in the solid ψ_S and in the solution ψ . Here \hat{u} is the normal unit vector on the interface Σ , and σ_s and ϵ'_s are the *static* conductivity and relative permittivity of the solid. We assume that in the low-frequency regime considered in this paper, the real dielectric constants and the conductivities of both the solid and the solution are frequency-independent.

Although, as mentioned above, the symmetry between anions and cations (*e.g.* having the same mobilities) is not essential to our results, it does afford a further simplification to the governing equations Eq. 3 and the BCs, as the dynamics of the total ion density $n^{\text{total}} = n_+ + n_-$ decouple from the driving field and it remains zero throughout the liquid and all the time. The net ion density follows a particularly simple equation, with a simple Green's function:

$$\nabla^2 n^{\text{net}} = \beta^2 n^{\text{net}}; \quad n^{\text{net}} = n_+ - n_-; \quad G(\vec{r}, \vec{r}') = -\frac{1}{4\pi} \frac{e^{-\beta|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}. \quad (5)$$

Here we introduce the Debye length λ that sets the scale for electrostatic screening in the solution, and a characteristic time scale τ_D :

$$\beta^2 \lambda^2 = 1 + i\omega\tau_D; \quad \lambda^2 = \frac{k_B T \epsilon_0 \epsilon'_w}{2Ne^2}; \quad \tau_D = \frac{\lambda^2}{D} = \frac{\epsilon_0 \epsilon'_w}{\sigma_w}. \quad (6)$$

Typical values of λ range from 0.3 nm to 10 nm from concentrated (1M) to dilute (10^{-3} M) electrolyte solutions, and τ_D ranges from 10^{-10} s to 10^{-7} s. In this paper we consider low-frequency $\omega\tau_D \ll 1$, so $\beta \approx 1/\lambda$.

II. A DILUTE SUSPENSION OF SPHERES: EXACT SOLUTION

For a single spherical particle of radius “ a ”, an exact solution can be found. Polarization P , defined by the far field potential $\psi(|\vec{r}| \gg a) \rightarrow P a^3 \vec{E}_0 \cdot \vec{r}/(|\vec{r}|^3) - \vec{E}_0 \cdot \vec{r}$, has a distinctive low frequency limit:

$$\omega\tau_D \ll \frac{\lambda \sigma_s}{a \sigma_w}, \quad \omega\tau_D \ll \frac{\lambda}{a}, \quad P \approx -\frac{1}{2} + \frac{3}{4} \frac{a}{\lambda} (i\omega\tau_D) \quad (7)$$

According to Maxwell-Garnett [24–27] effective medium approximation, for a dilute suspension of volume fraction $f \ll 1$, such that $f|P| \ll 1$, the effective complex dielectric constant ϵ_{eff} obeys the Clausius-Mossotti relation [26, 27]:

$$f P = \frac{\epsilon_{\text{eff}}/\epsilon_w(\omega) - 1}{\epsilon_{\text{eff}}/\epsilon_w(\omega) + 2}, \quad \epsilon_w(\omega) = \epsilon'_w + \frac{\sigma_w}{i\omega\epsilon_0}, \quad \frac{\epsilon_{\text{eff}}}{\epsilon_w(\omega)} \approx 1 + 3f P. \quad (8)$$

$$\epsilon'_{\text{eff}} \approx \epsilon'_w(1 + 3f P') + 3f \frac{\sigma_w}{\omega\epsilon_0} P'', \quad \tan \theta(\omega) \stackrel{\text{def}}{=} \frac{\epsilon'_{\text{eff}}}{\epsilon''_{\text{eff}}} \approx \frac{\epsilon'_{\text{eff}}}{\sigma_w/(\epsilon_0\omega)}. \quad (9)$$

P', P'' are the real and imaginary parts of P . $\epsilon'_{\text{eff}}, \epsilon''_{\text{eff}}$ are the real and imaginary parts of ϵ_{eff} . We also define here the phase shift $\theta(\omega)$ and use the fact that ϵ''_{eff} is dominated by the solution's $\epsilon''_w = \sigma_w/\omega\epsilon_0$.

Now, using the fact for electrolyte solution, $\sigma_w = \epsilon_0\epsilon'_w/\tau_D$, the real effective dielectric constant and the phase shift of the mixture is:

$$\frac{\epsilon'_{\text{eff}}(\omega \rightarrow 0)}{\epsilon'_w} = 1 - \frac{3}{2}f + \frac{9}{4}\frac{a}{\lambda}f, \quad \tan \theta = \frac{9f(\lambda/a)\omega\tau_D}{(2\lambda/a)^2 + (\omega\tau_D)^2(2\sigma_w/\sigma_s + 1)^2} \quad (10)$$

We see here that the imaginary part of the induced polarization P generates an enhancement a/λ to the dielectric constant of the mixture. For spheres whose $a \gg \lambda$, this enhancement, dependent only on their size, is very large. However, to observe such enhancement for larger spheres, one has to go to lower frequencies controlled by factor λ/a . Finally, if the particles are insulating, $\sigma_s = 0$, enhancement cannot be observed, as the first inequality in Eq. 7 can never be satisfied.

The phase shift expression in Eq. 10, also valid beyond the low-frequency of Eqs. 7, has a *size-independent* maximum of $(9/4)f/(1 + 2\sigma_w/\sigma_s)$ at $\omega\tau_D = (2\lambda/a)/(1 + 2\sigma_w/\sigma_s)$. For $\sigma_s \gg \sigma_w$, the maximum of $9f/4$ is easily observable by a commercial instrument, often with 0.1-milrad sensitivity, even for a very small volume fraction f .

III. SCALING LAW OF UNIVERSAL DIELECTRIC ENHANCEMENT

We now generalize the results for the dielectric enhancement of spheres in electrolyte solution, Eqs. 7, 10, to particles of arbitrary shapes, which we state in the form of three propositions that establish the universality, the scaling law and conditions for the enhancement. A final proposition demonstrates a scale-invariant maximum in the phase shift, easily accessible in impedance measurements.

Proposition 1. *For a homogeneous particle of any smooth, convex shape immersed in an electrolyte solution, driven by an external field $E_0 \hat{z} e^{i\omega t}$, as $\omega \rightarrow 0$ the total dipole moment, measured far from the particle, has the form $(\bar{\bar{P}}_r + (a/\lambda)i\omega\tau_D \bar{\bar{P}}_i) \vec{E}_0 V$. Here $\bar{\bar{P}}_r$ and $\bar{\bar{P}}_i$ are dimensionless rank two tensors depending solely on the shape, but not on the size or the electrical properties of the particle. “a” is the linear dimension of the particle and V is its volume.*

Proposition I generalizes the low frequency limit Eq. 7 of spherical particles. A natural corollary of it, which generalizes Eq. 10, gives the dielectric enhancement for a dilute, randomly oriented suspension of such particles under the effective medium theory.

Corollary I. *A dilute random suspension of identical particles in an electrolyte solution with volume fraction f will have a geometrically enhanced low-frequency real dielectric constant independent of the electrical properties of the particles: $\epsilon'_{\text{eff}} = \epsilon'_w(1 + f(P_r + (a/\lambda)P_i))$.*

P_r and P_i are dimensionless numbers depending solely on the particles’ shape, related to $\bar{\bar{P}}_r$ and $\bar{\bar{P}}_i$ in Proposition I by geometry.

The derivation of Corollary I from Proposition I is entirely analogous to the derivation Eq. 8 from Maxwell-Garnett theory [26, 27]. The only significant difference is that the particle’s shape being arbitrary, the polarization is no longer always colinear with the external field. This complication only introduces extra factors depending only on a particle’s shape [26] but does not change the scaling behavior of the imaginary part of the dipole moment, identical to that in Eq. 7 which leads to dielectric enhancement in Eq. 10. Random orientation of the particles ensures ϵ'_{eff} is a scalar.

The next proposition sets the conditions for observing the dielectric enhancement in Proposition I and Corollary I. They are generalizations of two inequalities in Eq. 7 of spherical particles.

Proposition II. *The conditions for observing the low-frequency dielectric enhancement in Proposition I and Corollary I are:*

$$\omega\tau_D \ll \frac{1}{R} \frac{\lambda}{a} \frac{\sigma_s}{\sigma_w}, \quad (11a) \quad \omega\tau_D \ll \frac{1}{R} \frac{\lambda}{a}. \quad (11b)$$

R is a dimensionless number, often of order one, determined solely by the shape of the particle. Its precise form will be shown in Appendix.

The scale-invariant maximum in the phase shift of Eq. 10 can also be generalized to

particles of arbitrary shapes:

Proposition III. *When $\sigma_w \ll \sigma_s$, the phase shift of a mixture in Corollary I, $\theta(\omega)$ as defined in Eq. 9, has a maximum $\tan \theta_{\max} = f \Theta$. Θ is a dimensionless number determined solely by the particle's shape.*

Next, we develop a physical picture of an Externally Induced Double Layer and translate it into two effective boundary conditions. We then use them to prove above propositions for arbitrary shapes.

IV. SEPARATION OF SCALES AND EFFECTIVE BOUNDARY CONDITIONS

In this section, we use two separations of scales, that the particle is large $a \gg \lambda$ and that the frequency is low $\omega\tau_D \ll 1$, to encode all the ion charge dynamics into two effective boundary conditions relating the solid phase and the charge neutral liquid phase.

Given that for $\omega\tau_D \ll 1$, $\beta = (1 + i\omega\tau_D)^{1/2}/\lambda \approx 1/\lambda$, the Green's function in Eq. 5 shows that any electrolyte net charge disturbance due to an introduced charge decays within a nano-scale length λ . Now consider any geometry where the minimal radius of curvature R_0 of any interface between the solid and the electrolyte solution is still much larger than λ . Under the driving field E_0 , the induced surface charges on the immersed bodies will in turn induce in the solution a *thin carpet of net charge* hugging the interface on the solution side, with thickness on the order of a few λ . We term this thin charged layer the “Externally Induced Double Layer” (EIDL), to distinguish it from the intrinsic double layer in the presence of a ζ -potential. Bazant and his co-workers used a similar term in another context [28]. The rest of the solution outside the EIDL will stay *charge neutral*.

For the rest of this paper, we use the subscript “*L*” for variables in the charge neutral-liquid *outside* the EIDL, and subscript “*S*” for variables *inside* the solids. Variables within the EIDL have no subscripts.

Given the large radius of curvature $R_0 \gg \lambda$, all spatial variations within the EIDL is much faster in the normal direction \hat{u} , so in the tangential directions the geometry can be modeled as a flat infinite plane. Other authors used similar approximations in finite ζ -potential models [11–13]. By Eq. 5, the net charge density in EIDL is

$$n^{\text{net}}(\xi) = n_0 e^{-\beta\xi}, \quad (12)$$

where n_0 is the net charge density right at the particle-solution interface and we set ξ -axis in the normal direction \hat{u} into the solution.

The electric field within the EIDL will vary much more rapidly in the normal than in the tangential direction, with the former typically on the scale $1/\lambda$ and latter $1/R_0$. Thus, the Poisson equation in the layer involves only the normal component of \vec{E} :

$$\vec{\nabla} \cdot \vec{E} \approx \frac{dE^\perp}{d\xi} = \frac{en^{\text{net}}(\xi)}{\epsilon_0\epsilon'_w}, \quad E^\perp(\xi) = E_L^\perp - \frac{e}{\epsilon_0\epsilon'_w} \int_\xi^\infty n^{\text{net}}(\xi') d\xi'. \quad (13)$$

Here E_L^\perp is the normal field in the charge-neutral fluid *just outside* the EIDL, corresponding to $\xi = +\infty$ since it lies at a distance $\gg \lambda$ away from the solid-solution interface.

According to Eq. 2, the net ion current density, predominantly in the normal \hat{u} direction within the EIDL, can be written as

$$j^{\text{EIDL}} = -D \frac{dn^{\text{net}}}{d\xi} + \frac{\sigma_w}{e} E^\perp = \underbrace{-D \frac{dn^{\text{net}}}{d\xi} - \frac{\sigma_w}{\epsilon_0\epsilon'_w} \int_\xi^\infty n^{\text{net}}(\xi') d\xi'}_{j^{\text{var}}} + \underbrace{\frac{\sigma_w}{e} E_L^\perp}_{j^{\text{out}}}. \quad (14)$$

The current in the EIDL is broken into two parts. One is the rapidly varying part j^{var} , due to the net ion density gradient and the electric field generated by the net charges in the EIDL. The other is a spatially constant, divergence-free current j^{out} due solely to the E_L^\perp carried over from the charge neutral, conductive liquid outside.

Since $n^{\text{net}}(\xi)$ vary spatially as $e^{-\beta\xi}$, as does its spatial derivatives and integrals, so does the rapidly varying current j^{var} due to them. Thus, charge conservation gives a starkly simple relation between the charge and current density:

$$\vec{\nabla} \cdot \mathbf{j} + \frac{\partial n^{\text{var}}}{\partial t} \approx \frac{dj^{\text{var}}}{d\xi} + \frac{\partial n^{\text{net}}}{\partial t} = -\beta j^{\text{var}} + i\omega n^{\text{net}} = 0, \quad j^{\text{var}} = \frac{i\omega}{\beta} n^{\text{net}}. \quad (15)$$

Naturally the spatially uniform current from the neutral liquid j^{out} does not contribute to the divergence of net particle current.

We can now relate the net charge distribution in the EIDL $n^{\text{net}}(\xi) = n_0 e^{-\beta\xi}$ to the electric field outside in the charge neutral liquid, by applying the crucial blocking boundary condition Eq. 4a that the net current vanishes at the solid-solution interface:

$$j^{\text{var}}(\xi = 0) + j^{\text{out}} = 0, \quad n_0 = -\frac{E_L^\perp \beta \sigma_w}{i\omega e}. \quad (16)$$

Now, integrating Poisson's equation in the EIDL Eq. 13 and using the charge distribution Eq. 12, we can obtain the normal electric field at $\xi = 0$, on the solution side:

$$E^\perp(\xi = 0) = E_L^\perp - \frac{e}{\epsilon_0\epsilon'_w} \int_0^\infty n(\xi') d\xi' = \left(1 + \frac{1}{i\omega\tau_D}\right) E_L^\perp. \quad (17)$$

A further integration of Poisson's equation gives the potential drop across the EIDL:

$$\psi_L - \psi(\xi = 0) = - \int_0^d d\xi' E^\perp(\xi) = -E_L^\perp \left(d + \frac{1}{i\omega\tau_D\beta} \right). \quad (18)$$

Here d is the “thickness” of the EIDL. Because the net charged density decays exponentially in a few λ , and the frequency $\omega \ll 1/\tau_D$, we have $1/(\omega\tau_D\beta) \approx \lambda/(\omega\tau_D) \gg d$, so we can drop d .

Combining Eq. 17 and Eq. 18, and using the boundary condition between the fluid and interface $\psi_S = \psi(\xi = 0)$ and $E_S^\perp = cE^\perp(\xi = 0)$ (Eq. 4b,c), we obtain the following effective boundary conditions (BCs) relating the fields and potentials *inside the solids directly* to those in the *charge neutral liquid outside EIDL*:

$$E_S^\perp = c \left(1 + \frac{1}{i\omega\tau_D} \right) E_L^\perp \quad \text{(a)}, \quad \psi_S = \psi_L + \frac{1}{i\omega\tau_D\beta} E_L^\perp. \quad \text{(b)}, \quad (19)$$

The BCs Eqs. 19 greatly simplify the original equations of motion in the first section. As the solid phase is electrically homogeneous, these BCs reduce coupled Poisson and Helmholtz equations in Eq. 1 and Eq. 5 to two independent Laplace equations. All the charge dynamics in the electrolyte solution, which is located exclusively in the EIDL, have been encoded in these two BCs. This enables us to apply results from the theory of harmonic functions to a solid-solution system, which we will resort to below.

The physics of Eq. 19a is made transparent by rewriting it as

$$\frac{E_S^\perp}{E_L^\perp} = c \left(1 + \frac{1}{i\omega\tau_D} \right) = \frac{\epsilon_0\epsilon'_w + \sigma_w/(i\omega)}{\epsilon_0\epsilon'_s + \sigma_s/(i\omega)} = \frac{\epsilon_w(\omega)}{\epsilon_s(\omega)}. \quad (20)$$

Here we use $\epsilon_{w,s}(\omega)$ to denote the frequency dependent complex dielectric constant in the solution and in solids at low frequency. Thus the BC Eq. 19a is nothing more than the generalization of the usual BC for normal AC electric fields on conductive boundaries, incorporating displacement currents, derived from charge conservation, with a form of conductivity proper to the electrolyte solution.

Eq. 19b, on the other hand, is clearly due to a dipole layer whose density is $-(\epsilon_0\epsilon'_w E_L^\perp)/(i\omega\tau_D\beta)$, which simple algebras show is exactly the effective dipole density of the EIDL $\int e n^{\text{net}}(\xi')\xi'd\xi'$. The difference between this dipole layer and the Gouy-Chapman double layer is simply that the dipole moment here is purely induced by, and is therefore proportional to, the external drive E_0 .

V. SIZE AND FREQUENCY SCALING: DIMENSIONAL ARGUMENTS

In this section, we give qualitative arguments, based purely on the analytical properties of dielectric responses and the form of the effective boundary conditions Eqs. 19a,19b, that severely constrain the form of the low-frequency limit of the dipole moment. The same arguments also show the scale invariance of the impedance phase shift maximum. We then outline a perturbation theory that computes this dipole moment but leave the mathematical details to the Appendix.

As is known from elementary electrodynamics, the fact that dielectric responses must be real in the time domain requires that the real part of the complex dielectric response function to be symmetric and the imaginary part antisymmetric under $\omega \rightarrow -\omega$. Furthermore, as the hydrodynamic flow is small and we have linearized the governing equations Eq. 3, the induced dipole moment will be purely linear to the external drive E_0 . Thus the most general form of the total dipole moment as $\omega \rightarrow 0$ is $(\tilde{P}_r + i\omega\tilde{P}_i)E_0$, with \tilde{P}_i, \tilde{P}_j independent of ω .

Furthermore, when $\omega\tau_D \ll (\epsilon'_w/\epsilon'_s)(\sigma_s/\sigma_w)$, the boundary condition Eq. 4c becomes dominated by conduction currents, and $c \approx i\omega\tau_D(\sigma_w/\sigma_{in})$ becomes purely imaginary. As $\omega\tau_D \ll 1$, the effective boundary conditions Eq. 19 take a starkly simple form:

$$E_S^\perp = \frac{\sigma_w}{\sigma_s} E_L^\perp \quad \text{(a)}, \quad \psi_S = \psi_L + \frac{1}{i\omega\tau_D\beta} E_L^\perp \quad \text{(b)}, \quad (21)$$

In this limit, in its *only* occurrence in the governing Laplace equation and BCs, ω appears in the combination $\omega\tau_D\beta \approx \omega\tau_D/\lambda$. Thus precisely this combination will appear in the imaginary term linear to ω in the total polarization P . Assume that the maximum of $\tan\theta(\omega)$ *exists*, which we will show in Appendix below, it will clearly have no dependence on ω . Yet the *only* occurrence of λ appears precisely in the *only* combination where ω occurs: $\omega\tau_D/\lambda$. Thus $\tan\theta_{\max}$, cannot have dependence on λ , either.

Finally, if we enlarge the linear dimension of the particle by a factor of α while preserving its shape, the boundary conditions, and thus the fields will remain the same provided we also rescale λ by α . Thus, the total dipole moment scales as the volume of the particle, and there is a prefactor a before $i\omega\tau_D/\lambda$ that scales linearly with the size of the particle, rendering the combination dimensionless. So the most general form of the total dipole moment as $\omega \rightarrow 0$ is $(P_r + (a/\lambda)i\omega\tau_D P_i)VE$, by virtues of the conduction dominated form of Eq. 21, and little more than dimensional analysis beyond that.

$\tan \theta_{\max}$, determined solely by the polarization P (Eq. 9) but having no dependence on λ , will depend on size “ a ” only through volume V , which is absorbed into f . So Θ in Proposition III is scale-invariant.

What remains to be shown is that the prefactors Θ, P_i, P_r does not depend on the material parameter σ_w/σ_s . We also need to answer the physically crucial question of the *conditions* under which the enhancement in Proposition and Corollary I are realized. One such condition Eq. 11a, for example, shows that insulating particles with $\sigma_s = 0$ cannot produce enhancement in our model without ζ -potential.

The EIDL dipole moment in Eq. 19b, proportional to E_L^\perp , is purely imaginary and out of phase. It becomes dominant at low frequency and is the cause of the dielectric enhancement there. Introduce a length scale $aR_S = |\psi_S/\hat{u} \cdot \vec{\nabla} \psi_S|$. Assume the maximum of R_S across the surface is around R . When $|\omega\tau_D\beta aR| \ll 1$, the second term in Eq. 21b dominates, making the EIDL dipole moment the main contributor to dielectric responses. This is partly the physics behind the condition Eq. 11b of Proposition II. Furthermore, if particles are insulating, $\sigma_s = 0$ forces the normal field E_L^\perp to zero, *eliminating* EIDL dipole moments altogether, partly explaining the condition Eq. 11b.

To make comparisons of scales like these more precise and useful, we use the Philips integral formulation of electrostatics [29] to combine Laplace equations and effective boundary conditions Eq. 21 into two *self-contained* integral equations *on the interface* between the solid and the charge neutral liquids. We then find a perturbative solution for the ψ_L integral equation at the $\omega \rightarrow 0$ limit and use Green’s theorem to compute the dipole moment explicitly from ψ_L on the interface. The conditions for the perturbative expansion are precisely those in Proposition II and the dipole moment has the form in Proposition I. The details can be found in the Appendix below, where we also show the *existence* of a maximum in the phase shift $\tan \theta(\omega)$.

VI. DISCUSSIONS

In this work we show that dielectric enhancement can happen in a mixture of non-insulating particles and electrolyte solution, with no ζ -potential on their ideally polarized, non-reactive interfaces. We also derive a universal scaling law for the magnitude of such enhancement. Our results comport well with preliminary data from recent experiments,

which show clear size-dependent dielectric enhancements in a conductive material with non-reactive surfaces. Furthermore, we show that if particles are much more conductive than the solution, for generic shapes there is always a *scale-invariant* maximum in the frequency-dependent phase shift in impedance measurements. Evidence of this is also observed in the preliminary data.

Beyond direct relevance to these experiments, our theory also opens up a wider range of candidates for applications involving dielectric enhancements. For example, materials of smaller ζ -potential can now be considered for inclusions in electrolyte solutions as contrast agents, particularly where electrochemically inert interfaces are advantageous, such as in biological applications. Furthermore, the scale invariance of the phase shift maximum means even sub-micron particles can produce large phase shifts at low volume fraction, opening the application of dielectric enhancement to intracellular probes.

The geometric scaling for the magnitude of dielectric enhancement may also prove useful for characterizing the statistical properties of the particles in complex fluids. For example, as we will show in another publication, the frequency dependence of the phase shift in a system of inhomogeneous spherical particles in solution can provide revealing information about the size distribution the particles.

Finally, the methods we develop here to prove the universal scaling of dielectric enhancement for arbitrary particle shapes may prove useful for studying other effects of interfacial processes in an electrolyte solution beyond the problem of dielectric enhancement. With a physical picture of externally induced dielectric enhancement (EIDL), we derive a pair of boundary conditions that are applicable to any interface that has small ζ -potential, not just that of particular suspensions. Examples of such interfaces include the oil in water emulsions in hydrocarbon productions or porous rocks soaked in saline solution. These boundary conditions encode all the complex charge dynamics on the interfaces, and reduce the physics away from the interfaces to that of simple charge-free electrostatics, tractable by a rich variety of traditional analytical and computational methods.

VII. APPENDIX: INTEGRAL EQUATION PERTURBATION THEORY

Here we tighten the scaling arguments above and derive a perturbative solution that shows prefactors $\overline{\overline{P}}_r, \overline{\overline{P}}_i$ in Proposition I to be material-independent. The two inequalities

in Eqs. 11a, 11b of Proposition II come about naturally as *conditions* for the perturbative expansions.

As boundary conditions Eqs. 19 incorporate all the free charge dynamics in the system, the potentials in the solid and the neutral liquid, on either side of the EIDL, obey Laplace equation and are *harmonic functions*. Using Stokes' Theorem, we can incorporate the BCs Eqs. 19 to compute the potential at *any point* \vec{r} *in space* solely from its *surface integrals* [29, 30], see also online SI.

$$\begin{aligned} \tilde{\epsilon}_\Omega \psi_\Omega(\vec{r}) &= \tilde{\epsilon}_L \psi_0(\vec{r}) \\ &\mp \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} [\tilde{\epsilon}_\Omega \psi_\Omega(\vec{r}'_\Sigma) - \psi_\Omega^{\text{eff}}(\vec{r}'_\Sigma)] \hat{u} \cdot \vec{\nabla}_{\vec{r}'_\Sigma} \frac{1}{|\vec{r} - \vec{r}'_\Sigma|} dS', \end{aligned} \quad (22)$$

$$\psi_\Omega^{\text{eff}} = \tilde{\epsilon}_{-\Omega} \psi_\Omega \pm \frac{1}{i\omega\tau_D\beta} \hat{u} \cdot \vec{\nabla} \psi_\Omega. \quad (23)$$

Here we use subscript $\Omega = S/L$ to label the Solid/(neutral) Liquid domain on either sides of the EIDL, which is considered infinitely thin and serves as boundary Σ . $-\Omega$ is the domain on the opposite side. We use *rescaled* dielectric constants $\tilde{\epsilon}_S = 1$ and $\tilde{\epsilon}_L = c(1 + 1/(i\omega\tau_D))$, a result of this integral formulation [30]. Under the mild assumption $\omega\tau_D \ll (\epsilon'_w/\epsilon'_s)(\sigma_s/\sigma_w)$, $\tilde{\epsilon}_L \approx \sigma_w/\sigma_s$ is real and frequency independent. $\psi_0 = -E_0 z$ is the “incident potential” due to the driving electric field. The \mp in Eq. 22 and \pm in Eq. 23 are for ψ_S and ψ_L respectively.

Now, letting \vec{r} approach Σ . The integral in Eq. 22 picks up new terms (the two terms before the \pm below) from the discontinuity of $\vec{\nabla}(1/|\vec{r} - \vec{r}'|)$ and we have [29, 30]:

$$\begin{aligned} \tilde{\epsilon}_L \psi_0(\vec{r}_\Sigma) &= \frac{1}{2} \tilde{\epsilon}_\Omega \psi_\Omega(\vec{r}_\Sigma) + \frac{1}{2} \psi_\Omega^{\text{eff}}(\vec{r}_\Sigma) \\ &\pm \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} [\tilde{\epsilon}_\Omega \psi_\Omega(\vec{r}'_\Sigma) - \psi_\Omega^{\text{eff}}(\vec{r}'_\Sigma)] \hat{u} \cdot \vec{\nabla}_{\vec{r}'_\Sigma} \frac{1}{|\vec{r}_\Sigma - \vec{r}'_\Sigma|} dS', \end{aligned} \quad (24)$$

Unlike Eqs. 22, Eqs. 24 are *self-contained integral equations* that fully determine ψ *on the surface* Σ , since both \vec{r}_Σ and \vec{r}'_Σ lie on Σ . In discussions below, if all positions \vec{r}, \vec{r}' lie on Σ we omit subscript Σ . It is important to note that the separate integral equations for ψ_S and ψ_L do not couple to one another. All physical influences from the other side of the EIDL have been encoded in the very form of ψ_{eff} .

Rescaling the potential inside the solid $\psi'_S = \psi_S/(i\omega\tau_D\beta a\tilde{\epsilon}_L)$, the integral equation Eq. 24

for ψ_S can be rewritten as:

$$\begin{aligned} \psi_0(\vec{r}) = & \frac{1}{2} \left[(1 + \tilde{\epsilon}_L)(i\omega\tau_D a\beta) + \frac{1}{R_S(\vec{r})} \right] \psi'_S(\vec{r}) \\ & + \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} \left[(1 - \tilde{\epsilon}_L)(i\omega\tau_D a\beta) - \frac{1}{R_S(\vec{r}')} \right] \psi'_S(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS'. \end{aligned} \quad (25)$$

Here, we introduce a new dimensionless shorthand variable:

$$R_S(\vec{r}) = \frac{1}{a \hat{u} \cdot \vec{\nabla} \psi_S(\vec{r})} = \frac{1}{a \hat{u} \cdot \vec{\nabla} \psi'_S(\vec{r})}, \quad R = \max_{\vec{r} \in \Sigma} (|R_S(\vec{r})|) \quad (26)$$

For a spherical particle, $R_S = 1$, but it generally varies across the interface. For the simplicity of presentation, we first assume the normal electric field never vanishes across the surface Σ : $|E_S^\perp| = |\hat{u} \cdot \vec{\nabla} \psi_S| > 0$. Since the electric field inside the solid and the linear size of the particle are both finite, ψ_S and ψ'_S are everywhere finite on surface Σ , so is R_S defined by Eq. 26. (This does not hold if the solid domain extends infinitely, as in macroscopically extended porous media.)

Now set the R in Eqs. 11a, 11b as the maximum of R_S across Σ (Eq. 26 above), simple algebra shows that if *both* conditions Proposition II are satisfied, the $1/R_S$ term in Eq. 25 dominates the integrals, and R_S can be self-consistently determined by a simpler equation:

$$\begin{aligned} \psi_0(\vec{r}) = & \frac{1}{2} \frac{1}{R_S(\vec{r})} \psi'_S(\vec{r}) - \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} \frac{1}{R_S(\vec{r}')} \psi'_S(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS' \\ = & \frac{a}{2} \hat{u} \cdot \vec{\nabla} \psi'_S(\vec{r}) - \frac{a}{4\pi} \oint\!\!\!\oint_{\Sigma} \hat{u} \cdot \vec{\nabla} \psi'_S(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS' \end{aligned} \quad (27)$$

Eq. 27 clearly does not depend on the electrical properties of the solid particle or the liquid. Nor does it depend on the frequency ω . The right hand side is furthermore invariant under a rescaling of the linear dimension of the particle $a \rightarrow \alpha a$, so ψ'_S is simply proportional to $\psi_0 \propto E_0 a$, with proportionality determined solely by particle shape. Thus R_S , and by extension R defined above, are determined solely by the *shape* of the solid particle.

Furthermore, as Eq. 27 is invariant with respect to rescaling a , and there is *no extra parameters* in the integral equation Eq. 27 other than the particle's shape, we expect that R_S will generally be of order one, as long as the particle's shape is smooth and convex, and its aspect ratios are near one (e.g. it is not shaped like a needle or a disc), so that there is no additional *geometric* parameters much smaller or larger than one.

Even when there are points on the surface where E_S^\perp vanishes, which is the case for a generic particle shape, the arguments above can be modified to preserve the validity of the

reduction of Eq. 25 to Eq. 27, as long as the places where $E_S^\perp = 0$ is a measure zero subset of the surface Σ , and near these points E_S^\perp approaches zero rapidly.

To see this most simply, imagine we discretize the surface Σ and make $\psi'_S(\vec{r}')$ into a column vector. The integral equation Eq. 25 will become a set of linear equations, with the kernel of the integral becoming a matrix and \vec{r}, \vec{r}' becoming column and row indices.

As $\omega \rightarrow 0$, the only matrix elements that *do not* trivially reduce to that of Eq. 27 are the rows labeled by \vec{r}' where E_S^\perp approaches zero, so that $1/R_S(\vec{r}')$ becomes small. However, since the points where E_S^\perp vanishes are a measure zero subset, and near them E_S^\perp declines rapidly, as $\omega\tau_D a\beta$ becomes smaller, the number of rows remaining significantly different between Eq. 25 and Eq. 27 rapidly becomes a negligible portion of the total matrix. So at a large enough R , which would be determined solely by the shape of the particle, the two integral kernels will converge, to the lowest order of parameter $\omega\tau_D a\beta$.

Having proved that R_S at low-frequency are determined by particle shape alone, we now use the two conditions in Proposition II, to define small parameters in a perturbative solution for the potential ψ_L , from which we derive an expression of the dipole moment in the form given in Proposition I and thus proving both propositions.

Combining the definition Eq. 26 and effective BCs Eq. 19, we can recast the effective potential ψ_L^{eff} in terms of R_S :

$$\psi_L^{\text{eff}} = \left(1 - \frac{1}{1 + (i\omega\tau_D\beta a R_S)\tilde{\epsilon}_L}\right) \psi_L \approx (i\omega\tau_D\beta a R_S\tilde{\epsilon}_L)\psi_L. \quad (28)$$

The last step uses an expansion of the fraction, which, as $\tilde{\epsilon}_L \approx \sigma_w/\sigma_s$, is valid when Eq. 11a of Proposition II holds. Of course, near the sets of point where $E_S^\perp = 0$ and R_S diverges, this approximation fail. But as discussed above, when $\omega\tau_D\beta a$ becomes sufficiently small, such points constitute a insignificant portion of the integral kernel.

With $\omega\tau_D\beta a R \ll 1$, which is the condition Eq. 11b in Proposition II, we can apply the following perturbative solution:

$$\begin{aligned} \tilde{\epsilon}_L \psi_0(\vec{r}) &= \frac{1}{2} (\tilde{\epsilon}_L + i\omega\tau_D\beta a R_S \tilde{\epsilon}_L) (\psi_L^0(\vec{r}) + \delta\psi_L(\vec{r})) \\ &- \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} (\tilde{\epsilon}_L - i\omega\tau_D\beta a R_S \tilde{\epsilon}_L) (\psi_L^0(\vec{r}') + \delta\psi_L(\vec{r}')) \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS', \end{aligned} \quad (29)$$

The electrical property of solids $\tilde{\epsilon}_L$ now cancels. The starting point ψ_L^0 is simply the solution

of this zeroth order order integral equation:

$$\psi_0(\vec{r}) = \frac{1}{2}\psi_L^0(\vec{r}) - \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} \psi_L^0(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS' \quad (30)$$

ψ_L^0 obviously is purely real. Since on the surface Σ the driving potential ψ_0 scales as $E_0 a$, so does ψ_L^0 . Furthermore, in Eq. 30, a rescaling of the particle size “ a ” will only affect ψ_0 , but not the integral kernel $\hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS'$, so $\psi_L^0(\vec{r}) = E_0 a p_r(\vec{r})$, where $p_r(\vec{r})$ is a *dimensionless* function determined *solely* by the *shape* of a particle.

We obtain the equation for the first order perturbation $\delta\psi_L$ by subtracting Eq. 30 from Eq. 29 and ignoring the second order terms:

$$\begin{aligned} & \delta\psi_L(\vec{r}) - \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} \delta\psi_L(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS' \\ &= -i\omega\tau_D\beta a \left[R_S(\vec{r})\psi_L^0(\vec{r}) + \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} R_S(\vec{r}')\psi_L^0(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS' \right]. \end{aligned} \quad (31)$$

Since ψ_L^0 is purely real, the imaginary part of the dielectric response P_i necessarily comes from the purely imaginary $\delta\psi_L$. The part in the square bracket on the right hand side in Eq. 31 scales linearly with ψ_L^0 and thus with $E_0 a$, but is otherwise entirely invariant to rescaling of particle dimension “ a ”. So, combined with the scaling for p_r above:

$$\psi_L(\vec{r}) = \psi_L^0(\vec{r}) + \delta\psi_L(\vec{r}) = E_0 a [p_r(\vec{r}) + (i\omega\tau_D\beta a) p_i(\vec{r})], \quad (32)$$

where $p_i(\vec{r}), p_r(\vec{r})$ are, again, *dimensionless* functions determined *solely* by the *shape* of the particle.

Now we return to Eq. 22. When $|\vec{r}| \gg |\vec{r}'_{\Sigma}|$, $\vec{\nabla}_{\vec{r}'_{\Sigma}} \frac{1}{|\vec{r} - \vec{r}'_{\Sigma}|} \approx \frac{\vec{r}}{|\vec{r}|^3}$. The expansion in Eq. 28 also greatly simplifies the surface integral:

$$\begin{aligned} \psi_L(\vec{r}) &= \psi_0(\vec{r}) + \frac{1}{4\pi\epsilon_0} \frac{\vec{r} \cdot \vec{P}}{|\vec{r}|^3} \\ &= \psi_0(\vec{r}) + \frac{\vec{r}}{4\pi|\vec{r}|^3} \cdot \oint\!\!\!\oint_{\Sigma} \psi_L (1 - i\omega\tau_D\beta a R_S) \hat{u} dS'. \end{aligned} \quad (33)$$

Thus, the dipole moment \vec{P} can be simply read off, from the behavior of ψ_L at large \vec{r} , as the surface integral in Eq. 33. When the two conditions Eq. 11a,11b in Proposition II are satisfied, $\psi_L \approx \psi_L^0 + \delta\psi_L$. The real and imaginary part are in turns defined by integral equations Eq. 30,31, well-posed Fredholm equations of the second kind [30].

Applying the scaling behaviors of ψ_L^0 and $\delta\psi$ in Eq. 32, we have the following scaling of the dipole integral in Eq. 33:

$$\begin{aligned} & \oint\!\!\!\oint_{\Sigma} \psi_L (1 - i\omega\tau_D\beta a R_S) \hat{u} dS' \\ & \approx E_0 a \oint\!\!\!\oint_{\Sigma} [p_r(\vec{r}'_{\Sigma}) + (i\omega\tau_D\beta a)(p_i(\vec{r}'_{\Sigma}) - R_S p_r(\vec{r}'_{\Sigma}))] \hat{u} dS' \end{aligned} \quad (34)$$

Since p_r, p_i and R_S are dimensionless functions determined solely by particles' shape, their surface integrals scale as a^2 , and the dipole moment scales as $E_0 a^3 \propto E_0 V$. As the polarization is not necessarily collinear with $E_0 \hat{z}$, its final form is $(\bar{\bar{P}}_r + (a/\lambda)i\omega\tau_D \bar{\bar{P}}_i) \vec{E}_0 V$, just as in Proposition I.

Finally, we outline a proof of the existence of a maximum in the phase shift defined in Eq. 9. At low frequencies, dielectric enhancement dominates P and $|\tan\theta(\omega)| \approx (a/\lambda)f\omega\tau_D|P_i|$ is a fast increasing function of ω . At larger ω , we show in online SI, by methods similar to those in this Appendix, that P is real and has no enhancement, generating $\tan\theta(\omega) = (1 + f P_r)\omega\tau_D \approx \omega\tau_D$. It is then easy to find θ_L, θ_H , from the low and high frequency regimes, such that $|\tan\theta_L| > |\tan\theta_H|$. Thus $|\tan\theta(\omega)|$, initially increasing and then decreasing, must have a maximum. The details are given in online SI.

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VIII. SUPPORTING INFORMATION

A. Model Validity Conditions

In this section, we address the three conditions for our analysis in the main text: the limit on the driving field E_0 , the validity for ignoring the hydrodynamic flow due to electro-osmosis and the limit on ζ -potential. Our derivations of these conditions focus on the low frequency, universal enhancement regime discussed in the main text, but most can be generalized to a broader frequency range.

Our approach is based on self-consistency arguments, in which we show that, under the conditions given in the main text, the solution of our simplified, linear model is also the solution of the more complete model under discussion. Such arguments rely on the uniqueness of solutions of the complete model, which is reasonable physically, because the dielectric responses of random suspensions in electrolyte solution are not known to exhibit bistable behaviors. We will not, however, attempt mathematical proofs for such uniqueness here.

1. Linearization Condition: $eE_0a \ll k_B T \Rightarrow n_{\pm} \ll N_0$

We begin by deriving the condition for linearizing the charge conservation equations Eq. 2. As we note in the main text, for symmetric ions, we have $n^{\text{total}} = n_+ + n_- = 0$ throughout the electrolyte solution, so $|n_{\pm}| = (1/2)n^{\text{net}}$. Thus we only need to prove $|n^{\text{net}}| \ll N_0$ throughout the electrolyte solution.

Of course, n^{net} is non-zero only within the EIDL. Furthermore, as shown in the main text, it decays exponentially away from the solid-solution interfaces, so we only need to prove $n_0 \ll N_0$, where n_0 is defined in Eq. 16 in the main text. Thus we have:

$$\frac{1}{2} \frac{|n_0|}{N_0} = \frac{|E_L^{\perp} \beta \sigma_w|}{\omega N_0 e} = \frac{|E_L^{\perp} \beta| e}{\omega \tau_D k_B T} \lambda^2 = \frac{e |\psi_{\text{EIDL}}|}{k_B T} \lambda^2 |\beta|^2 \approx \frac{e |\psi_{\text{EIDL}}|}{k_B T}. \quad (35)$$

Here we use the fact that $\sigma_w = \epsilon_0 \epsilon'_w / \tau_D$, Eq. 16 relating n_0 to E^{\perp} and the definition of λ in Eq. 6. We also introduce the $\psi_{\text{EIDL}} = \psi_L - \psi_S$, which is the potential drop within the EIDL and use the effective BC in Eq. 19b to relate ψ_{EIDL} to E_L^{\perp} .

At low frequency, the potential on the surfaces just outside the EIDL $\psi_L \approx \psi_L^0$, which is the zeroth-order solution defined by the integral equation Eq. 30. As discussed in the main text, $\psi_L^0 = E_0 a p_r(\vec{r})$, and p_r is a dimensionless function determined solely by the shape of the particle via Eq. 30.

As long as the particle is smooth, convex and has an aspect ratio not too far from one (*i.e.* not shaped like a disk or needle), we expect the integral equation gives $p_r(\vec{r})$ of order one throughout the surface Σ of the particle, as there is no singularity or *geometric* parameters that are much bigger or smaller than one. Thus we expect the potential on the surface to be of the order $\psi_L \sim E_0 a$.

A comparison with the Philips integrals for ordinary dielectrics [29] shows that, at this limit, the external potential ψ_L^0 is approximately that outside a particle with $\epsilon' = 0$. If the particle is smooth and of aspect ratio not far from one, we expect the electric field around the particle to be comparable to E_0 (and has no component normal to the particle surface). As we generally set the origin of the potential to be inside the particle, on its surface the potential ψ_L is of the order $E_0 a$.

For the internal potential, we begin by noting that ψ'_S , as given by Eq. 27, is clearly proportional to E_0 as ψ_0 does. Moreover, a rescaling of particle size $a \rightarrow \alpha a$ will result in $\psi'_S \rightarrow \alpha \psi_S$. Thus $\psi'_S \propto E_0 a$, with the proportionality constant determined entirely by the shape of the particle, with no extra length scale like λ in Eq. 29. Thus we expect for particles with smooth, convex surface and aspect ratios not far from one, $\psi'_S \sim E_0 a$, so $|\psi_S| = |i\omega\tau_D\beta a\epsilon_L\psi'_S| \ll E_0 a$ because we are at such a low frequency that $\omega\tau_D \ll (\lambda/a)(\sigma_s/\sigma_w) \approx |1/(\beta a\epsilon_L)|$.

So we have across the surface Σ , $\psi_{\text{EIDL}} = \psi_L - \psi_S \sim E_0 a$. Thus by Eq. 35 when $eE_0 a \ll k_B T$, we have $|n_{\pm}| \ll N_0$ and the linearization in the main text is valid.

2. The Insignificance of the Electrophoresis Flow

For electrokinetic flow, we continue the planar approximation by which we derive the effective BCs in the EIDL and use the classic Helmholtz-Smoluchowski formula for planes [22]:

$$|v_{\text{max}}^{\parallel}| = \frac{\epsilon_0 \epsilon'_w}{\eta} E^{\parallel} |\psi_{\text{slip}} - \psi(\xi = 0)| \leq \frac{\epsilon_0 \epsilon'_w}{\eta} E^{\parallel} |\psi_{\text{EIDL}}|. \quad (36)$$

Here η is the dynamic viscosity of water and v_{\max}^{\parallel} is the maximum relative velocity the solution reaches. E^{\parallel} is the electric field tangential to the particle surface, and it varies relatively slowly within the EIDL compared with the normal field. ψ_{slip} is the potential at the slipping plane in the EIDL. Since in our EIDL, the potential drop monotonically decreases, the maximum amount of potential drop within it is ψ_{EIDL} , as defined above. The maximum ionic current associated with the electro-osmosis flow is thus $j_{\max}^{\text{drag}} = v_{\max}^{\parallel} N_0$.

Let us compare this with the conductive current due to the electric field E^{\parallel} , $j^{\text{cond}} = E^{\parallel} \sigma_w / e = E^{\parallel} \epsilon_0 \epsilon'_w / e \tau_D$, which is but one component of the ionic current considered in Eq. 2. The ratio between the two is:

$$\frac{|j^{\text{drag}}|}{|j^{\text{cond}}|} \leq \frac{e |\psi_{\text{EIDL}}| N_0}{\eta / \tau_D} \ll \frac{k_B T N_0}{\eta / \tau_D} \approx 0.134. \quad (37)$$

The last ratio turns out to be independent of N_0 after taking into account of the N_0 dependence of τ_D . In the last step we used the following material parameters: $D = 2 \times 10^{-9} \text{m}^2/\text{s}$, $T = 300\text{K}$, $\eta = 8.9 \times 10^{-4} \text{Pa} \cdot \text{s}$. Thus the electrokinetic flow is much smaller than the conductive flow in the planar, linearized EIDL approximation of our model.

3. ζ -potential is unimportant for $e\psi_{\zeta} \ll k_B T$

We show in this subsection that when the ζ -potential $e\psi_{\zeta} \ll k_B T$ the equations of motion for the time-dependent physics reduces to that of Eq. 3 and produces the same enhancement as in the main text.

We begin by analyzing the physics under finite ζ -potential in the static limit without the external drive $E_0 \hat{z} \exp(i\omega t)$. We still assume the minimal radius of curvature of all interfaces are much larger than the Debye length λ , so the interfaces are considered infinite planes and the problem reduced to that of 1D. The system is assumed to be in local equilibrium, so that the density currents \vec{j}_{\pm} , as defined in Eq. 2, are everywhere zero and the ion densities follow the Boltzmann distribution. The equations of motion are then:

$$N_{\pm} = N_0 e^{\mp \frac{e\psi}{k_B T}}, \quad \nabla^2 \psi_0 \approx \frac{d^2 \psi}{d\xi^2} = -\frac{e(N_+ - N_-)}{\epsilon_0 \epsilon'_w}. \quad (38)$$

Here N_0 is the ion density in the charge-neutral liquid outside the double layer. The solution of this equation is well-known [11].

$$\frac{e\psi_0(\xi)}{k_B T} = 2 \ln \left(\frac{1 + t e^{-\xi/\lambda}}{1 - t e^{-\xi/\lambda}} \right), \quad t = \tanh \left(\frac{e\psi_{\zeta}}{4k_B T} \right). \quad (39)$$

When the ζ -potential is small, $e\psi_\zeta \ll k_B T$, $t \ll 1$:

$$\frac{e\psi_0(\xi)}{k_B T} \approx e^{-\xi/\lambda}, \quad N_\pm(\xi) = N_0^\pm e^{-\xi/\lambda}, \quad N_0^\pm = N_0 e^{\mp e\psi_\zeta/k_B T} \approx N_0. \quad (40)$$

Now we turn on the external field $E_0 \hat{z} \exp(i\omega t)$. We write the time-dependent solution as $N_\pm^t = N_\pm + n_\pm$ and $\psi^t = \psi_0 + \phi$. We assume here *only* that $n_\pm \ll N_\pm \approx N_0$, which is the same as the linearization condition discussed above. *We do not assume the potential change ϕ is small compared with ψ .*

Using Eq. 38, it is easy to see that Poisson equation preserves its form for n_\pm and ϕ :

$$\nabla^2 \phi = -\frac{e(n_+ - n_-)}{\epsilon'_w \epsilon_0}. \quad (41)$$

The ionic density currents are more complicated because of the cross terms, but using the fact that the static ionic currents are zero anywhere, and $n_\pm \ll N_0 \approx N_\pm$, we have:

$$\vec{j}_\pm = -D \left(\vec{\nabla} N_\pm \pm \frac{eN_\pm}{k_B T} \vec{\nabla} \psi \right) = 0, \quad \left| \frac{en_\pm}{k_B T} \vec{\nabla} \phi \right| \ll \left| \frac{eN_\pm}{k_B T} \vec{\nabla} \phi \right|, \quad (42)$$

and the time-dependent current densities simplify:

$$\begin{aligned} \vec{j}_\pm^t &= -D \left(\vec{\nabla} N_\pm^t \pm \frac{eN_\pm^t}{k_B T} \vec{\nabla} \psi^t \right) \\ &\approx -D \left(\vec{\nabla} n_\pm \pm \left(\frac{en_\pm}{k_B T} \vec{\nabla} \psi + \frac{eN_0}{k_B T} \vec{\nabla} \phi \right) \right) \end{aligned} \quad (43)$$

Now assume ϕ is the potential inside the double layer that, like those of the solution in the main text, varies spatially as $\psi_{\text{EIDL}} \exp(-\xi/\lambda)$. Because when the ζ -potential is weak $e\psi_\zeta \ll k_B T$, the potential ψ inside the double layer is $\psi_\zeta \exp(-\xi/\lambda)$ (Eq. 40), the two conductive current terms in Eq. 43 can be easily compared:

$$\frac{en_\pm/k_B T |\vec{\nabla} \psi|}{eN_0/k_B T |\vec{\nabla} \phi|} = \frac{e\psi_\zeta/k_B T n_\pm}{e\psi_{\text{EIDL}}/k_B T N_0} = \frac{e\psi_\zeta}{k_B T} \frac{n_\pm/N_0}{e\psi_{\text{EIDL}}/k_B T} \quad (44)$$

According to Eq. 35, the second factor is approximately two, and by assumption the first is much smaller than one. Thus, the time dependent current densities have forms completely analogous to Eq. 2 in the main text:

$$\vec{j}_\pm^t \approx -D \left(\vec{\nabla} n_\pm \pm \frac{eN_0}{k_B T} \vec{\nabla} \phi \right). \quad (45)$$

Combining Poisson equation Eq. 41 and currents Eq. 45, one see that when the ζ -potential is small, ϕ and n_\pm follows exactly the equations of motion in the main text.

Furthermore, the equations for ψ, ϕ and for N_{\pm}, n_{\pm} completely decouple, and the physics is determined by the linear superposition of the two. The static solution ψ_0 obviously only makes a real, frequency-independent contribution to the total polarization, so when $e\psi_{\zeta} \ll k_B T$, the ζ -potential does not change the dielectric enhancement described in the main text.

B. Asymmetric Ions

In the main text, we have made the simplifying assumption that the ions are symmetric, with cation and anion having not only the same charge, but also the same diffusion coefficient. The second assumption is clearly unrealistic. In this section we show that relaxing these two assumptions do not change the physical picture in the main text.

Assume the diffusion coefficient of the cations and anions are D_+, D_- , their charges are $q_+, -q_-$, and their density outside the EIDL are N_+, N_- . Also assume that outside EIDL the liquid is charge neutral: $N_- q_- = N_+ q_+$. The total and net particle densities no longer separate naturally, so Eq. 5 no longer hold. Instead, we have

$$\begin{aligned} \nabla^2 n_+ &= (\alpha_+ + \frac{1}{\lambda_+^2}) n_+ - \frac{1}{\lambda_-^2} n_-, \quad \alpha_{\pm} = \frac{i\omega}{D_{\pm}}, \\ \nabla^2 n_- &= -\frac{1}{\lambda_+^2} n_+ + (\alpha_- + \frac{1}{\lambda_-^2}) n_-, \quad \lambda_{\pm}^2 = \frac{k_B T \epsilon_0 \epsilon'_w}{N_{\pm} q_{\pm}^2}. \end{aligned} \quad (46)$$

On the other hand, the boundary condition Eq. 4 are still best expressed in terms of $n^{\text{total}} = n_+ + n_-$ and $n^{\text{net}} = n_+ - n_-$:

$$\begin{aligned} \hat{u} \cdot \vec{\nabla} n^{\text{net}} &= -\frac{2\epsilon_0 \epsilon'_w}{\lambda_{\pm}^2 q_{\pm}} \hat{u} \cdot \vec{\nabla} \psi \\ \hat{u} \cdot \vec{\nabla} n^{\text{total}} &= 0 \end{aligned} \quad (47)$$

The obvious way forward is to make linear combinations of n_{\pm} to make Eq. 46 diagonal. To keep algebras and notations manageable and the physics transparent, here we focus on the case where the ions have the same charge $q_+ = q_- = q$ (hence $N_+ = N_- = N_0, \lambda_+^2 = \lambda_-^2 = 2\lambda^2$) but different diffusion coefficients. Under these transformations:

$$\begin{aligned} n^{\text{net}} &= -\lambda^2 \alpha_2 \rho_1 + (1 - \lambda^2 \alpha_1) \rho_2, \quad \alpha_1 = \frac{1}{2} (\alpha_+ + \alpha_-) \\ n^{\text{total}} &= (1 + \lambda^2 \alpha_1) \rho_1 + \lambda^2 \alpha_2 \rho_2, \quad \alpha_2 = \frac{1}{2} (\alpha_+ - \alpha_-), \end{aligned} \quad (48)$$

the equations of motion are diagonal:

$$\begin{aligned}\nabla^2 \rho_1 &= \left(\frac{1}{\lambda^2} + \alpha_1 \right) \rho_1, \\ \nabla^2 \rho_2 &= \alpha_1 \rho_2, \\ \nabla^2 \psi &= -\frac{q}{\epsilon_0 \epsilon'_w} n^{\text{net}}.\end{aligned}\tag{49}$$

Combining Eq. 47–49, and following the derivation of the EIDL approximation in the main text, one can recover the following effective BCs analogous to Eq. 19:

$$\begin{aligned}E_S^\perp &= c \left(1 + \frac{1}{i\omega\tilde{\tau}} \right) E_L^\perp, \\ \psi_S &= \psi_L + \frac{1}{i\omega\tilde{\tau}\tilde{\beta}} E_L^\perp,\end{aligned}\tag{50}$$

where we redefine the parameters τ_D and β as following

$$\tilde{\tau} = \frac{\lambda^2}{\tilde{D}}, \quad \tilde{\beta}^2 = \frac{1}{\lambda^2} (1 + i\omega\bar{\tau}), \quad \bar{\tau} = \frac{\lambda^2}{\overline{D}},\tag{51}$$

and \overline{D} and \tilde{D} are the harmonic and arithmetic mean of the two diffusion constants:

$$\overline{D} = \frac{2}{1/D_1 + 1/D_2}, \quad \tilde{D} = \frac{D_1 + D_2}{2}.\tag{52}$$

The case of ions with unequal charges proceed similarly, albeit with much more complicated redefinitions of τ and β . But the form of the effective BCs remain those of Eqs. 50.

Of course, with boundary conditions like Eqs. 50, reasoning about dielectric enhancement identical to those in the main text can be carried out, with identical conclusions and merely redefined parameters.

C. Derivation of the Philips Integral Formulation

To derive the Philips integral equation formulation for our BCs Eq. 21, we use the fact that potentials on both side of the EIDL obey Laplace equation, and make use of the following form of the Stokes' theorem for a harmonic function to compute its value anywhere in a domain Ω from its value on its boundary \vec{r}'_Σ :

$$\begin{aligned}& \int_\Sigma \left(A(\vec{r}'_\Sigma) \hat{u} \cdot \vec{\nabla}_{\vec{r}'_\Sigma} B(\vec{r}, \vec{r}'_\Sigma) - \hat{u} \cdot \vec{\nabla}_{\vec{r}'_\Sigma} A(\vec{r}'_\Sigma) B(\vec{r}, \vec{r}'_\Sigma) \right) dS' \\ &= \begin{cases} A(\vec{r}) \quad \forall \vec{r} \in \Omega, \\ 0 \quad \forall \vec{r} \notin \Omega. \end{cases}\end{aligned}\tag{53}$$

Here $B = -\frac{1}{4\pi} \frac{1}{|\vec{r}-\vec{r}'|}$ is the Green's function of the Laplace operator. $A(\vec{r})$ is a harmonic function that is non-zero in a simply-connected domain Ω and zero elsewhere, and the *surface* integral is carried out on \vec{r}'_{Σ} which lies on the boundary $\Sigma = \partial\Omega$. Any variable with subscript Σ lies on Σ . \hat{u} is a unit normal vector pointing *out of* the domain Ω . In this section the boundary Σ is set to the EIDL, which is considered to be infinitely thin compared with the solid and neutral liquid domains.

Let function ψ_S coincide with the potential in the solid and be zero in the neutral liquid outside the EIDL, and function ψ_L coincide with the potential in the neutral liquid and be zero within the solid. To apply Eq. 53 to the unbounded domain in the neutral liquid, the function $A(\vec{r})$ need to vanish quicker than $1/r^2$ at infinity. Thus we need to subtract from ψ_L (and ψ_S for symmetry reason) the “incident” potential $\psi_0 = -E_0 z$ due to the external drive. Set $A = \psi_S/\epsilon_L - \psi_0$ and again $A = \psi_L - \psi_0$, then Eq. 53 for a point \vec{r} lying *inside the solid* become

$$\begin{aligned} \frac{\psi_S(\vec{r})}{\tilde{\epsilon}_S} - \psi_0(\vec{r}) &= \frac{1}{4\pi} \oint_{\Sigma} \left\{ \left[\frac{\psi_S(\vec{r}'_{\Sigma})}{\tilde{\epsilon}_S} - \psi_0(\vec{r}'_{\Sigma}) \right] \hat{u} \cdot \vec{\nabla}_{\vec{r}'_{\Sigma}} \frac{1}{|\vec{r} - \vec{r}'_{\Sigma}|} \right. \\ &\quad \left. - \left[\hat{u} \cdot \vec{\nabla}_{\vec{r}'_{\Sigma}} \psi_S(\vec{r}'_{\Sigma})/\tilde{\epsilon}_S - \hat{u} \cdot \vec{\nabla}_{\vec{r}'_{\Sigma}} \psi_0(\vec{r}'_{\Sigma}) \right] \frac{1}{|\vec{r} - \vec{r}'_{\Sigma}|} \right\} dS', \end{aligned} \quad (54)$$

$$\begin{aligned} 0 &= \frac{1}{4\pi} \oint_{\Sigma} \left\{ \left[\psi_L(\vec{r}'_{\Sigma}) - \psi_0(\vec{r}'_{\Sigma}) \right] \hat{u} \cdot \vec{\nabla}_{\vec{r}'_{\Sigma}} \frac{1}{|\vec{r} - \vec{r}'_{\Sigma}|} \right. \\ &\quad \left. - \left[\hat{u} \cdot \vec{\nabla}_{\vec{r}'_{\Sigma}} \psi_L(\vec{r}'_{\Sigma}) - \hat{u} \cdot \vec{\nabla}_{\vec{r}'_{\Sigma}} \psi_0(\vec{r}'_{\Sigma}) \right] \frac{1}{|\vec{r} - \vec{r}'_{\Sigma}|} \right\} dS', \end{aligned} \quad (55)$$

Subtract the two equations. Use BC Eq. 19a $\hat{u} \cdot \vec{\nabla} \psi_S/\tilde{\epsilon}_L = \hat{u} \cdot \vec{\nabla} \psi_L$ to cancel the second terms inside the integral. Then use BC Eq. 19b to eliminate ψ_L , with $\hat{u} \cdot \vec{\nabla} \psi_L$ being substituted by $\hat{u} \cdot \vec{\nabla} \psi_S$ via Eq. 19a. One then arrives at Eq. 24 for ψ_S , expressing the value of ψ_S inside the solid by its value on the boundary. The same can be done for a point \vec{r} lying *in the charge neutral liquid*, which gives the equivalent expression for $\psi_L(\vec{r})$.

Eq. 22 and Eq. 23 are identical to that of the simple dielectric. The only difference is the extra term due to the dipole moment in the EIDL $1/(i\omega\tau_D\beta) \hat{u} \cdot \vec{\nabla} \psi_{\Omega}$, which produces the dielectric enhancement.

Finally, the derivation of Eq. 24 from Eq. 22, by taking the \vec{r} to the surfaces, is standard. The only subtlety is the singularity of the kernel $\vec{\nabla}(1/|\vec{r}-\vec{r}'|)$, which is equivalent to that of a dipole layer on the interface Σ . For a smooth surface, this singularity contribute an

extra term equal to $\pm 1/2$ times the value of the function multiplying the kernel at point \vec{r} [29, 30], depending the direction of the normal vector \hat{u} .

D. Scale Invariant Maximum in the Impedance Phase Shift

We first note that condition $\sigma_s \gg \sigma_w$ is not very restrictive in real world applications, because even rather strong electrolyte like sea water and human blood has conductivity of the order a few S/m . Not only any metal, but common engineering materials like amorphous carbon and moderately doped semiconductor have several orders of magnitude higher conductivities than the electrolyte solution.

Secondly, when $\sigma_s \gg \sigma_w$, the condition Eq. 11a allows a much wider frequency range than Eq. 11b. All our discussions, including the “high-frequency” regime below, happen under the range of Eq. 11a (*c.f.* Eq. 59). Under this condition, the expansion Eq. 28 of the effective potential for ψ_L is valid, so there is always the cancellation of $\tilde{\epsilon}_L$ in Eq. 29. This means that the material property of the particle σ_s/σ_w drops out of the integral equation for ψ_L so anything determined by the dipole moment P will be material independent. This shows that the frequency-dependent phase shift angles $\tan \theta(\omega)$ is independent of σ_s/σ_w at the frequencies where Eq. 11a hold.

At low frequency when conditions in Eqs. 11a, 11b are satisfied, the enhanced part of polarization, due to the imaginary part of the dipole moment P_i , dominates, so

$$|\tan \theta(\omega)| \approx (a/\lambda)\omega\tau_D|P_i| f \quad (56)$$

increase monotonically with ω . Thus, if we can show that at a larger frequency, $|\tan \theta(\omega)|$ decrease in value, there must be a maximum in a frequency between.

At higher frequency, consider the following conditions:

$$\omega\tau_D \gg \frac{1}{R'} \frac{\lambda}{a} [\mathbf{a}], \quad \omega\tau_D \ll \frac{\sigma_s}{\sigma_w} \frac{\epsilon_w}{\epsilon_s}, 1 [\mathbf{b}], \quad R' = \min_{\vec{r} \in \Sigma} |R_S(\vec{r})|. \quad (57)$$

R_S is defined in Eq. 26 in the main text. When both conditions in Eq. 57b hold, $\epsilon_L \approx \sigma_w/\sigma_s \ll 1$. Under condition Eq. 57a, we also have, across the interface, $|\hat{u} \cdot \vec{\nabla} \psi_S / (i\omega\tau_D\beta)| \ll |\psi_S|$. Combining the two, we have $|\psi_S^{\text{eff}}| \ll |\psi_S|$. Upon a simple rescaling $\psi'_S = \psi_S/\tilde{\epsilon}_L$, which does not affect R_S (see Eq. 26), the integral equation Eq. 24 for ψ'_S again reduces to a very

simple form:

$$\psi_0(\vec{r}) = \frac{1}{2}\psi'_S(\vec{r}) + \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} \psi'_S(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS' \quad (58)$$

It is easy to see that under these conditions R_S , and by extension R' , are again determined solely by a particle's shape. As argued in the main text, for smooth, convex shapes whose aspect ratios are not too far from one, we expect R' to be of order one.

Now turn to ψ_L under this limit. Since $\tilde{\epsilon}_L \ll 1$, we can find a frequency that satisfies

$$1 \ll |i\omega\tau_D\beta a R_S| \ll 1/\tilde{\epsilon}_L \quad (59)$$

across the interface (except, again, those point where R_S diverges, which as we have argued in the main text can be ignored if we choose $|\omega\tau_D\beta a|$ sufficiently far from the upper limit ϵ_L). At such a frequency, the form of the effective potential Eq. 28 remains true, so we still have:

$$\begin{aligned} \psi_0(\vec{r}) &= \frac{1}{2} (1 + i\omega\tau_D\beta a R_S) \psi_L(\vec{r}) \\ &\quad - \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} (1 - i\omega\tau_D\beta a R_S) \psi_L(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS', \end{aligned} \quad (60)$$

But now, by Eq. 57a, the effective potential term is dominant. Thus, after introducing a rescaling $\psi'_L = \psi_L(i\omega\tau_D\beta a)$, we can again transform the integral equation into a very simple form:

$$\psi_0(\vec{r}) = \frac{1}{2} R_S(\vec{r}) \psi'_L(\vec{r}) + \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} R_S(\vec{r}') \psi'_L(\vec{r}') \hat{u} \cdot \vec{\nabla}_{\vec{r}'} \frac{1}{|\vec{r} - \vec{r}'|} dS'. \quad (61)$$

By same scaling arguments in the main text, we expect $\psi'(\vec{r}) = E_0 a p(\vec{r})$, where p is a dimensionless function determined solely by particle's shape.

At high frequency described in Eq. 57a, the dipole integral analogous to Eq. 33 in our case is:

$$\begin{aligned} \psi_L(\vec{r}) &= \psi_0(\vec{r}) + \frac{1}{4\pi} \oint\!\!\!\oint_{\Sigma} \psi_L (1 - i\omega\tau_D\beta a R_S) \hat{u} \cdot \frac{\vec{r}}{|\vec{r}|^3} dS' \\ &\approx \psi_0(\vec{r}) - \frac{1}{4\pi} \frac{\vec{r}}{|\vec{r}|^3} \cdot \oint\!\!\!\oint_{\Sigma} \psi'_L(\vec{r}') R_S(\vec{r}') \hat{u} dS'. \end{aligned} \quad (62)$$

By the same argument in the main text, the polarization at this limit will scale as $E_0 a^3 = E_0 V$. And it will obviously be purely real, as ψ'_L and $p(\vec{r})$ are purely real.

More important, any additional length scale, such as λ in the imaginary part of polarization in the enhancement regime in Eq. 32, is absent here. Indeed, if the particle's surface is smooth, convex and its aspect ratios not too far from one, there is no additional very small or very large *geometric* parameters in Eq. 61, so we expect the polarization in this limit, upon orientation averaging, to be of the form $E_0 V P$, where P is a real, dimensionless number *of order one*, independent of both frequency and material parameters. Thus, in this limit, $\epsilon'_{\text{eff}} = \epsilon'_w(1 + f P) \approx \epsilon'_w$ and

$$\tan \theta(\omega) \approx \omega \tau_D. \quad (63)$$

Because of the large factor $(a/\lambda) f$ in Eq. 56 and its absence in Eq. 63, it should not be difficult to find a frequency ω_L in the regime Eqs. 11a, 11b and a frequency ω_H in the regime Eqs. 59 such that $\tan \theta(\omega_L) > \tan \theta(\omega_H)$. This will prove that the function $\tan \theta(\omega)$ decreases after initially increasing monotonically and thus have a maximum between ω_L and ω_H .

To be more precise, assume we have

$$\omega_{L,H} \tau_D = \frac{\lambda}{a} A_{L,H}, \quad A_L \ll \frac{1}{R}, \quad \frac{1}{R'} \ll A_H \ll \frac{\sigma_s}{\sigma_w}. \quad (64)$$

Here R and R' are defined in Eq. 26 and Eq. 57. Then we have

$$\frac{|\tan \theta(\omega_L)|}{|\tan \theta(\omega_H)|} \approx \frac{(a/\lambda) f |P_i| \omega_L \tau_D}{\omega_H \tau_D} = f |P_i| \frac{a}{\lambda} \frac{A_L}{A_H}. \quad (65)$$

The factors in front of A_L/A_H is essentially the size of dielectric enhancement factor at low frequency, which, as we mention in the abstract, can easily amount to 10^4 even for a very dilute electrolyte solution. If we can assume that, for smooth, convex particles with aspect ratios not too far from one, because there is no additional *geometric* small or large parameters far from one, both R and R' are not far from one, it should thus be not difficult to find a pair A_L, A_H that satisfies both Eq. 64 and the condition $A_H/A_L < f |P_i| (a/\lambda)$, which, as discussed above, guarantee a maximum for the phase shift $|\tan \theta(\omega)|$ between ω_L and ω_H . As we note above, this maximum will be independent of the material parameter σ_s/σ_w .

Finally, we want to show that the three approximations we use to derive the equations of motion and the effective BCs Eqs. 19 are still valid in the high frequency regime Eq. 57, 59, 64. According the first section of this Online Support Information, the key is to prove that the potential drop across the EIDL ψ_{EIDL} is comparable or smaller than $E_0 a$.

For ψ_L on the charge neutral solution side, we have $\psi'_L = \psi_L(i\omega\tau_D\beta a)$ obeys Eq. 61. As we argue above, $\psi'_L = E_0 a p(\vec{r})$ where $p(\vec{r})$ is a dimensionless function determined solely by the shape of the particle. If the particle is smooth, convex and has aspect ratio not far from one, we expect $p(\vec{r})$ to be of order one. Thus, ψ_L is of order $|E_0 a|/|\omega\tau_D\beta a|$ on the interface. Assuming R' , as defined in Eq. 57, is of order one, as we have argued above from Eq. 58, Eq. 57a implies $|\omega\tau_D\beta a| \gg 1$ and thus $\psi_L \ll E_0 a$.

On the other hand, similar argument suggest that for the internal potential, ψ'_S defined in Eq. 58 is also of order $E_0 a$ across the interface, meaning the potential on the solid side of the EIDL $\psi_S = \tilde{\epsilon}_L \psi'_S \ll E_0 a$, given that $\tilde{\epsilon}_L = \sigma_w/\sigma_s \ll 1$.

Combining the estimates for ψ_L and ψ_S we have $|\psi_{\text{EIDL}}| = |\psi_L - \psi_S| \ll E_0 a$ and thus all three assumptions for deriving our linearized equation of motions hold at the frequency range of ω_H in Eq. 64 above.